

4. Dilution Cooling

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The dilution refrigerator

Liquid helium-4 has a boiling point of 4.2 K. For studies of superconductors, superfluids and other applications, it is necessary to go down to milli- or micro-Kelvins.

Evaporation of helium-4 liquid can lower the temperature, but only to about 1.3 K. Below this temperature, the vapour pressure is so small that very little would evaporate.

It is possible to overcome this limitation using a mixture of liquid helium-3 and liquid helium-4. The way is to “evaporate” pure liquid helium-3 into the mixture.

This is done in the dilution refrigerator. Using this method, it is possible to reach into the milliKelvin range.

Learning Aims: You will learn to

Sketch and explain the phase diagram of a mixture of liquid helium-3 and liquid helium-4.

Describe and explain the how the combination of concentrated and dilute phases of the mixture lead to cooling.

Explain why dilution cooling can reach much lower temperature than evaporation cooling.

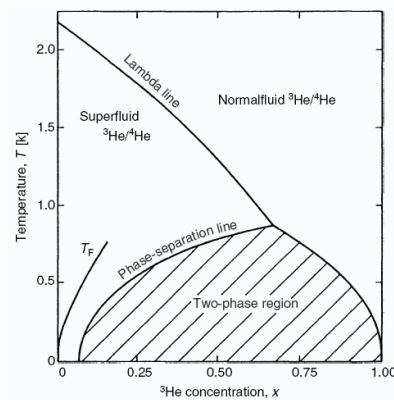
Explain how and why the mixture can be treated as a Fermi gas. Derive the cooling power.

Sketch and explain the dilution refrigerator.

Properties of the liquid ^3He - ^4He mixtures

Liquid ^3He - ^4He Mixtures

Start with the phase diagram of a mixture of liquid helium-3 and liquid helium-4.. This tells us how the mixture behaves at different concentrations and temperatures.

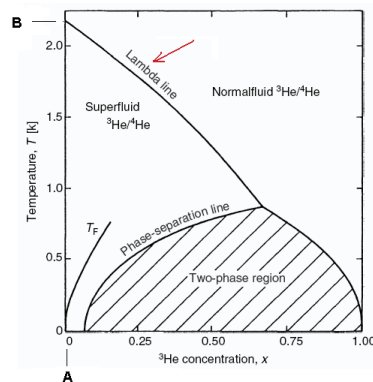


D.S. Betts: An Introduction to Millikelvin Technology (Cambridge University Press, 1989).
J. Wilks, D.S. Betts: An Introduction to Liquid Helium, 2nd edn. (Clarendon, Oxford 1987)

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The Phase Diagram

The Lambda line indicates the temperature at which superfluid transition takes place for a given x .

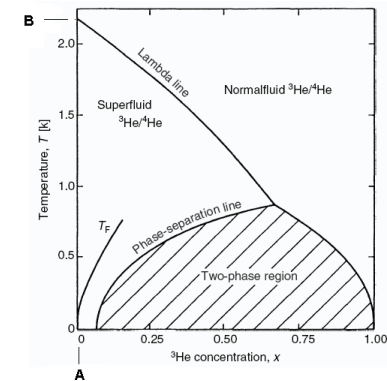


At point B: At $x = 0$, the Lambda line shows that superfluid transition takes place at the temperature $T = 2.2$ K.

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The Phase Diagram

Let x be the fraction of ^3He atoms in the ^3He - ^4He mixture. In the figure, x is the horizontal axis.

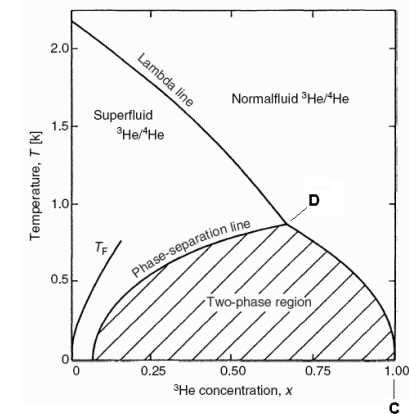


At point A: $x = 0$ means pure ^4He .

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The Phase Diagram

At point C: $x = 1$ is pure ^3He .

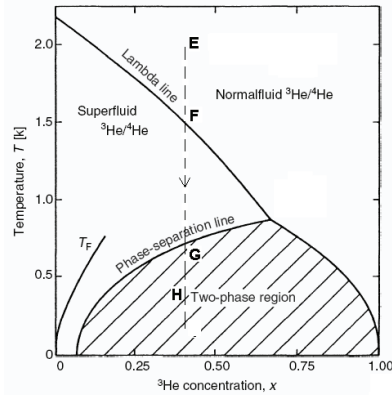


At point D: The Lambda line stops at the shaded region. So it is not clear if pure ^3He (at C) can become superfluid. In fact it can, at the much lower temperature of 2.5 mK.

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The Phase Diagram

Along the dashed line: Suppose we start with a mixture at a concentration and temperature at point E. When this is cooled down to the temperature at point F, it would change to a superfluid.

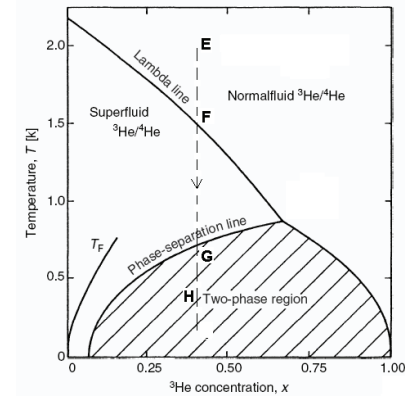


If it is cooled further, it would reach the shaded region at G. What if it is cooled below that to a temperature at point H?

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The Phase Diagram

The shaded region is meant to indicate that it is not possible for the mixture to exist at a concentration and temperature in that region.

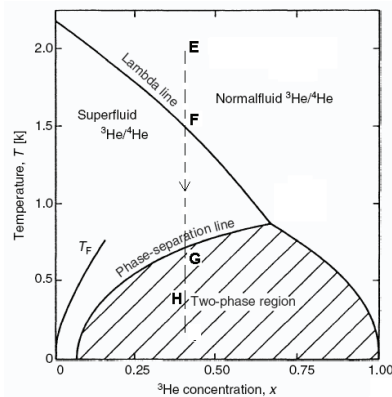


For a temperature at point H, it is only possible to have concentrations that are either smaller than that at point J, or higher than at point K.

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The Phase Diagram

So if a mixture is cooled down to a temperature at H, it would separate into two layers.



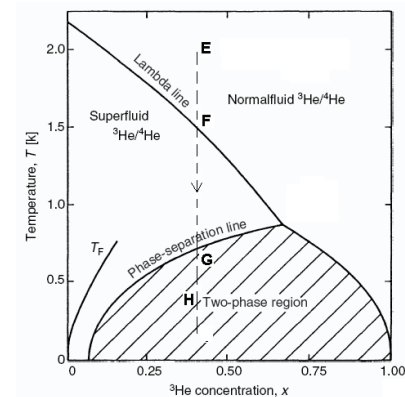
One layer has the concentration at J, and the other layer has the concentration at K.

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The Phase Diagram

At J, the concentration x of ^3He is lower, and the mixture is called the dilute phase.

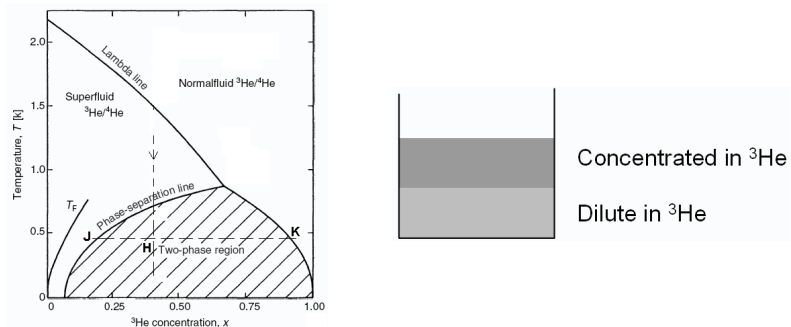
At K, the concentration is higher, and it is called the concentrated phase.



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The Phase Diagram

Because ^3He is less dense than ^4He , the concentrated phase floats on top of the dilute phase.

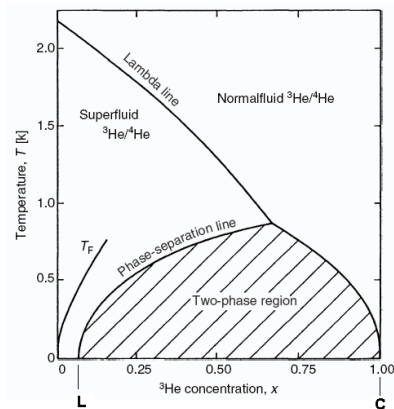


Note that the dilute phase is superfluid, whereas the concentrated phase is normal fluid.

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The Phase Diagram

At point L: Note that in the dilute phase, the solubility of ^3He would remain 6.6% even as the temperature approaches 0 K.

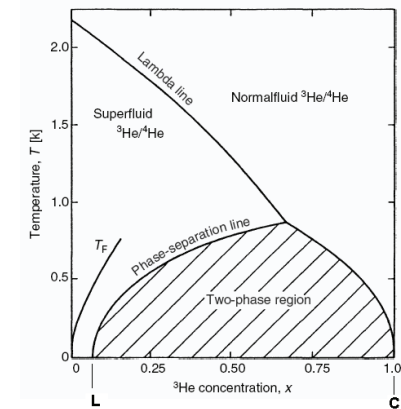


This is the property that makes the dilution refrigerator possible.

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The Phase Diagram

At point L: When we reach a temperature below 0.1 K, the highest concentration possible is $x = 6.6\%$.



If we start at a higher temperature and concentration and cool down below 0.1 K, it would always separate into 2 layers:

1. One layer has 6.6% concentration in ^3He - at L.
2. The other is nearly pure ^3He - at C.

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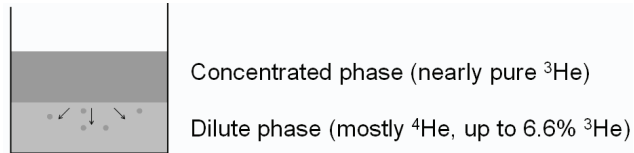
Cooling by dilution

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Cooling by dilution

Suppose that we start with a layer of pure helium-3 floating on a layer of pure helium-4 at 0.1 K.

Helium-3 would diffuse into the helium-4 layer below. The reverse would not happen, as we know from the phase diagram.



When this happens, the temperature would fall.

We may compare this to evaporation. Instead of vaporising to a vacuum above, the helium-3 “vaporises” into the liquid below.

In this case, it is really mixing instead of evaporation.

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Cooling power

We have previously seen that the vapour pressure of helium falls exponentially with decreasing temperature.

The vapour pressure, P , is directly related to the rate at which the helium atoms vaporise from the liquid. Therefore it is also directly related to the rate of removing heat from the liquid:

$$\dot{Q} \propto P \propto e^{-1/T}$$

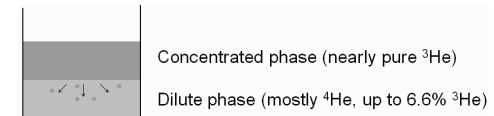
\dot{Q} is also called the cooling power, and is used to compare the performance of different refrigerators.

So the cooling power of the evaporation refrigerator falls exponentially with decreasing temperature.

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Cooling by dilution

By mixing into the lower layer, the helium-3 above is effectively being diluted. Hence the term “dilution cooling.”



This continues, and the concentration of helium-3 in the in the bottom layer increases until it reaches 6.6%. Then the mixing stops.

In order to continue cooling, we must somehow remove the helium-3 dissolved in the dilute phase. This also has an analogy with cooling by evaporation, where we have to pump out the vapour to prevent it from being saturated.

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Cooling power

In dilution cooling, the helium-3 concentration, x , in the dilute phase is directly related to the rate at which helium-3 leaves the concentrated phase.

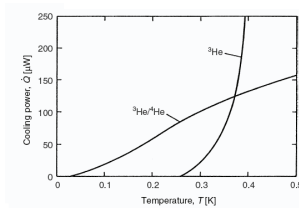
To determine the rate at which heat is removed, we must consider the heat change of mixing, ΔH . As we shall see later, this heat change is proportional to T^2 .

The cooling power of helium-3 dilution is therefore

$$\dot{Q} \propto x \Delta H \propto T^2$$

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The figure compares the cooling power of helium-3 evaporation, and ^3He - ^4He dilution, for the same helium-3 circulation rate.



assuming the same helium gas circulation rate of 5 l s^{-1}

O.V. Lounasmaa: Experimental Principles and Methods Below 1K (1974)

From previous reasonings, we can understand why the cooling power for the evaporation falls much faster than that for dilution.

Below 0.3 K, the dilution refrigerator clearly has a much higher cooling power than the evaporation refrigerator.

 ^3He - ^4He mixtures as Fermi liquids

It is possible to derive the heat change of mixing. This would be useful for estimating the cooling power.

Helium-3 has nuclear spin $I = 1/2$. It is a fermion. It obeys the Fermi-Dirac statistics. So we hope that the same formula for the heat capacity of electrons can be used for the ^3He - ^4He mixture:

$$C_3 = \frac{\pi^2 T}{2 T_F} R \text{ at } T \ll T_F$$

where C_3 denotes the heat capacity of helium-3.

From the lectures on electrons in metal, we have seen that the Fermi temperature $T_F = E_F/k_B$, and the Fermi energy is

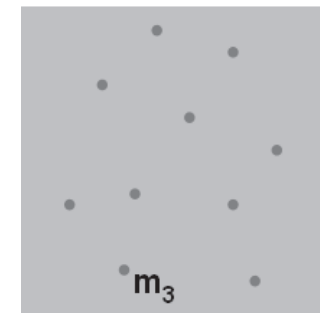
$$E_F = \frac{\hbar^2}{2m_3} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

where m_3 denotes the mass of the helium-3 atom.

 ^3He - ^4He mixtures as Fermi liquids

 ^3He - ^4He mixtures as Fermi liquids

The problem with the formulae for electrons is that they are derived assuming that the particles do not interact with one another.



This assumption is not valid here. In the dilute phase, the helium-3 atoms are very close to the helium-4. In the concentrated phase, the helium-3 are very close to themselves.

It turns out that the helium-3 atoms in the dilute phase can be modelled as heavier particles in a vacuum.



For example, at 6.6% concentration, if we use a value of $2.45m_3$ for the mass of helium-3 instead of the actual m_3 , the formulae would still give a reasonable answer.

The higher mass is called the effective mass, and often denoted by m^* .

For pure helium-3, $m^* = 2.78m_3$.

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Heat change of mixing

Another point to note for the formula

$$C_3 = \frac{\pi^2 T}{2 T_F} R \text{ at}$$

is the condition that $T \ll T_F$.

For electrons in metal, we have seen that the Fermi energy is much higher than $k_B T$ at room temperature.

What is the Fermi temperature for helium-3 in the dilute phase? Is it still higher than the temperature we are interested in?

At 6.6% concentration, and using the effective mass of $m^* = 2.45m_3$, we would find using the formulae that T_F is about 1 K.

The dilution refrigerator typically operates below 0.1 K. This should be well within the valid range for the Fermi gas formulae.

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Heat change of mixing

To derive the heat change of mixing, we need a few ideas and formulae from thermodynamics. Since the movement of particles from concentrated to dilute phase is essentially a change in phase, we need the condition for phase equilibrium:

$$\mu_C = \mu_D$$

where μ is the chemical potential, subscript C is for concentrated phase, and D for the dilute phase.

The chemical potential is given by

$$\mu = H - TS$$

where H is the enthalpy per mole, and S the entropy per mole of the phase.

I shall start with a quick summary on the basic physics behind the equilibrium condition.

The enthalpy H is given by

$$H = U + pV,$$

where U is the internal energy, p the pressure and V the volume. So

$$\mu = H - TS = U + pV - TS.$$

The equilibrium equation is a statement that the change in chemical potential if one phase is changed to the other, is zero. This may also be expressed as:

$$\Delta\mu = \Delta U + p\Delta V - T\Delta S = 0.$$

This assumes that pressure and temperature are the same in both phases.

There would always be a pressure and a temperature gradient in the refrigerator, since the concentrated phase is being cooled and it is on top. But since the volumes are small and the two phases are in close contact, we shall assume that it is approximately true.

Returning to the equilibrium condition

$$\mu_C = \mu_D,$$

since $\mu = H - TS$, we may write this as

$$H_C - TS_C = H_D - TS_D$$

Remember that subscript C is for concentrated phase, and D for the dilute phase. The enthalpy change of mixing is therefore:

$$H_D - H_C = TS_D - TS_C$$

This is the heat change of mixing that we want to estimate.

To do so, we need to find the entropies S_C and S_D in both phases.

The equilibrium condition is:

$$\Delta U + p\Delta V - T\Delta S = 0.$$

To understand this physically, note that for a reversible change, $T\Delta S = \Delta Q$, the heat input. $p\Delta V$ is the work done by one phase if it expands on changing to the other phase.

So the left hand side is a statement that the total energy of one mole of a phase remains the same, when it changes into another phase.

If this is the case, then the two phases would remain in equilibrium.

If, on the other hand, there is a net release in energy when one phase changes into the other, then this change would take place, and there would be no equilibrium.

We need the entropy in each phase. This can be determined from the specific heat capacity as follows.

Conservation of energy, or the first law of thermodynamics, tells us that:

$$dQ = dU + dW$$

dW is the mechanical work done - by expansion or contraction. Since we have a liquid, the volume change is very small. If we neglect this, we have

$$dQ = dU$$

Since $dS = dQ/T$, the entropy is given by integrating:

$$\int dS = \int \frac{dQ}{T}.$$

To carry out the integration, replace T and S in the integral by dummy variables first:

$$\int dS' = \int \frac{dQ}{T'}.$$

Next, we must set the limits. The limits for T' are just 0 K and T .

When temperature is 0 K, entropy is zero, according to the 3rd law of thermodynamics. When temperature is T , let the entropy be S . So

$$\int_0^S dS' = \int_0^T \frac{dQ}{T'}.$$

This can be writing in terms of heat capacity C :

$$S = \int_0^T \frac{dQ}{T'} = \int_0^T \frac{dU}{T'} = \int_0^T \frac{C}{T'} dT'$$

where the left hand side has been integrated and gives S . In order to obtain the entropy, we need know the heat capacity as a function of temperature.

In the dilute phase, the specific heat for helium-3 may be estimated by the Fermi gas formula

$$C_3 = \frac{\pi^2}{2} \frac{T}{T_F} R$$

Suppose that the concentration of the mixture in a dilution refrigerator is close to 6.6%. Using the effective mass of $m^* = 2.45m_3$, and the formula for the Fermi energy, we would get

$$C_3 = 106T \text{ J/(mol K)}$$

So the entropy for helium-3 in the dilute phase is

$$S_D = \int_0^T \frac{C_3(T')}{T'} dT' = \int_0^T 106 dT' = 106T \text{ J/(mol K)}$$

Heat capacity for pure helium-3 is known from measurements taken at temperatures below 40 mK:

$$C_3 \approx 22T \text{ J/(mol K)}$$

Entropy for the concentrated phase is therefore

$$S_C = \int_0^T \frac{C_3(T')}{T'} dT' = \int_0^T 22 dT' = 22T \text{ J/(mol K)}$$

In principle, we can use the same way to find the entropy for helium-3 in the dilute phase. However, we would need this for different concentrations, and not many measurements are available.

We have seen earlier that the specific heat formulae for a Fermi gas can be used ...

We have obtained the entropies in the two phases:

$$\begin{aligned} S_C &= 22T \text{ J/(mol K)} \\ S_D &= 106T \text{ J/(mol K)} \end{aligned}$$

We can now find the heat change of mixing:

$$H_D - H_C = T(S_D - S_C) = T(106T - 22T) = 84T^2 \text{ J/mol}$$

Note that this change is positive. This implies an increase in internal energy.

Because of conservation of energy, heat energy has to be absorbed from the surrounding. Hence the cooling.

The cooling power is then

$$\dot{Q} = n_3 \Delta H = n_3 (H_D - H_C) = 84 n_3 T^2 \text{ W}$$

where n_3 is the number of moles per second of helium-3 moving from concentrated to dilute phase.

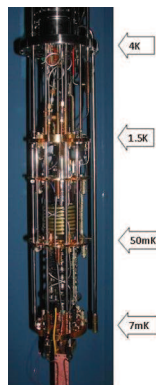
The cooling power is proportional to T^2 , as we have seen early on.

For typical values of $n_3 = 100 \mu\text{mol s}^{-1}$ and $T = 10 \text{ mK}$, we find

$$\dot{Q} = 1 \mu\text{W}.$$

Examples of dilution refrigerators

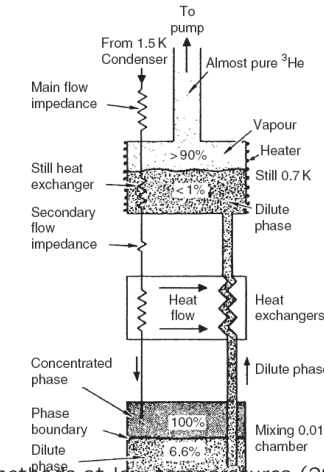
This is a dilution refrigerator used in the semiconductor physics group in the Cambridge physics department.



<http://www.phy.cam.ac.uk/research/sp/cryo.php>

You should be able to tell from the temperatures indicated what the various parts are.

This is a schematic diagram. It would be housed inside a vacuum chamber that is immersed in a helium-4 bath at 4.2 K.



Pobell, Matter and methods at low temperatures (2007)

Learning Outcome: You should be able to

Sketch and explain the phase diagram of a mixture of liquid helium-3 and liquid helium-4.

Describe and explain the how the combination of concentrated and dilute phases of the mixture lead to cooling.

Explain why dilution cooling can reach much lower temperature than evaporation cooling.

Explain how and why the mixture can be treated as a Fermi gas. Derive the cooling power.

Sketch and explain the dilution refrigerator.

Worked Examples

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Solutions

(i) There is 6% of a mole of helium-3 in the mixture.

So the number of helium-3 atoms is

$$0.06 \times N_A = 3.612 \times 10^{22}.$$

(ii) Formula for Fermi energy is

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}.$$

Mass of helium-3 atoms = $3m_u$ Effective mass, $m = 2.4 \times 3m_u$
number of helium-3 atoms, $N = 0.06 \times N_A$. volume of 1 mole
of mixture, $V = 30 \text{ cm}^{-3} = 30 \text{ m}^{-6}$.

Substituting, we find $E_F = 4.996 \times 10^{-24} \text{ J}$.

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Example 1

Suppose that one mole of liquid helium-3/helium-4 mixture has a volume of 30 cm^{-3} . This mixture contains 6% of helium-3.

(i) Find the number of helium-3 atoms in this mixture.

(ii) Assume that the helium-3 behaves as a Fermi gas, and that each helium-3 atom has an effective mass ratio of 2.4. Find the Fermi temperature.

(iii) Write down the formula for heat capacity of the mixture. Find the heat capacity at 20 mK.

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So Fermi temperature, $T_F = E_F/k_B = 0.3620 \text{ K}$.

(iii) Formula for heat capacity is

$$C = \frac{\pi^2}{2} R \frac{T}{T_F}.$$

At $T = 20 \text{ mK}$, and substituting T_F , we find $C = 2.266 \text{ J/K}$.

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Example 2

Suppose that one mole of pure liquid helium-3 has a volume of 30 cm^{-3} .

(i) Find the number of helium-3 atoms in this liquid.

(ii) Assume that the helium-3 behaves as a Fermi gas, and that each helium-3 atom has an effective mass ratio of 2.8. Find the Fermi temperature.

(iii) Write down the formula for heat capacity of this liquid. Find the heat capacity at 20 mK.

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(iii) Formula for heat capacity is

$$C = \frac{\pi^2}{2} R \frac{T}{T_F}.$$

At $T = 20 \text{ mK}$, and substituting T_F , we find $C = 0.4051 \text{ J/K}$.

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Solutions

(i) There is one mole of helium-3.

So the number of helium-3 atoms is $N_A = 6.02 \times 10^{23}$.

(ii) Formula for Fermi energy is

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}.$$

Mass of helium-3 atoms = $3m_u$ Effective mass, $m = 2.8 \times 3m_u$
number of helium-3 atoms, $N = N_A$. volume of 1 mole, $V = 30 \text{ cm}^{-3} = 30 \text{ m}^{-6}$.

Substituting, we find $E_F = 2.794 \times 10^{-23} \text{ J}$.

So Fermi temperature, $T_F = E_F/k_B = 2.025 \text{ K}$.

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Example 3.

A layer of pure liquid helium-3 floats on top of a layer of liquid helium-3/helium-4 mixture at 20 mK. The mixture contains 6% of helium-3.

(i) Assume that the entropy in each layer is numerically equal to the heat capacity. Using results from the previous two questions, write down the entropy of each layer.

(ii) When one mole of liquid helium-3 from the top layer mixes into the bottom layer, there is heat exchange. Write down the formula for the heat change of mixing in terms of entropy in each layer.

(iii) Find the heat change when one mole of liquid helium-3 from the top layer mixes into the bottom layer. Explain why there is a cooling effect.

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Solutions

(i)

Entropy of 1 mole of mixture at bottom, $S_D = C = 2.266 \text{ J/K}$.

Entropy of 1 mole of pure helium-3 on top, $S_C = C = 0.4051 \text{ J/K}$.

(ii)

$$\Delta Q = T \Delta S.$$

So heat change of mixing is

$$\Delta H = T(S_D - S_C).$$

(iii) $T = 20 \text{ mK} = 0.020 \text{ K}$

Substituting,

$$\Delta H = T(S_D - S_C) = 0.03721 \text{ J}$$

This is a positive overall increase in energy of the two layers. It must come from heat absorbed from surrounding. That is why there is a cooling effect.